

## BEST AVAILABLE COPY

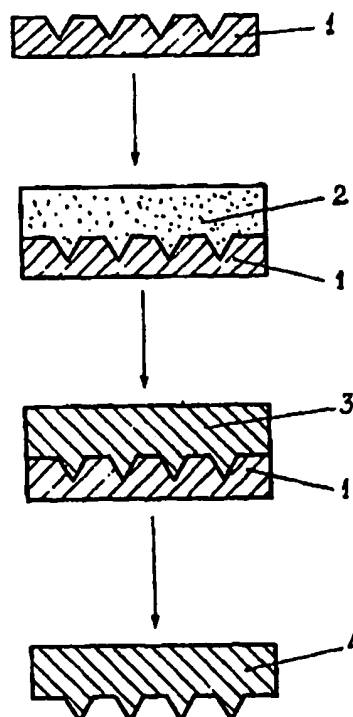


PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|  |   |   |
|--|---|---|
| (51) International Patent Classification <sup>6</sup> :<br><b>H01J 1/30, 9/02</b>  | <b>A1</b>   | (11) International Publication Number: <b>WO 99/34385</b><br>(43) International Publication Date: <b>8 July 1999 (08.07.99)</b> |
| <p>(21) International Application Number: <b>PCT/EP98/08403</b></p> <p>(22) International Filing Date: <b>22 December 1998 (22.12.98)</b></p> <p>(30) Priority Data:<br/>           97121538                      23 December 1997 (23.12.97)    RU<br/>           98120500                      18 November 1998 (18.11.98)    RU</p> <p>(71) Applicant (for all designated States except US): <b>ALFAR INTERNATIONAL LTD. (IE/IE); 20 Clan William Terrace, Dublin 2 (IE).</b></p> <p>(72) Inventors; and<br/>           (75) Inventors/Applicants (for US only): <b>GORDEEV, Sergey Konstantinovich [RU/RU]; Apartment 27, Rybatskij Prospect 19/1, St.Petersburg, 193076 (RU). RALCHENKO, Victor Grigorejevich [RU/RU]; House 6, Apartment 188, Gorkij Street, Kaliningrad, 141170 (RU). ZHUKOV, Sergey Germanovich [RU/RU]; House 8, Apartment 41, Tjermysjevskij Square, St.Petersburg, 196070 (RU). KARABUTOV, Alexander Vladimirovich [RU/RU]; House 8a, Apartment 72, Tjemiahovskij Street, Severnij Area, Moscow, 153829 (RU). BELOBROV, Peter Ivanovich [RU/RU]; House 2, Apartment 8, Akademgorodok, Krasnojarsk, 660036 (RU). NEGODAEV, Michael Alexandrovich</b></p> | <p>[RU/RU]; House 122A, Apartment 69, Oktiaborskij Prospect, Luberts, 140005 (RU).</p> <p>(74) Agents: <b>HYLTNER, Jan-Olof et al.; AB Dahls Patentbyrå, P.O. Box 606, S-182 16 Danderyd (SE).</b></p> <p>(81) Designated States: <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b><br/> <i>With international search report.<br/>           Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> |   |
| <p>(54) Title: <b>A FIELD ELECTRON EMITTER AND A METHOD FOR PRODUCING IT</b></p> <p>(57) Abstract</p> <p>The present invention relates to a field electron emitter consisting of diamond and graphite-like carbon. According to the present invention said emitter has within its volume a uniform composition of diamond particles bonded by graphite-like carbon. The present invention also relates to a method of manufacturing such a field electron emitter by heat treating an intermediate body in gaseous hydrocarbon.</p>  |   |   |



*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

|    |                          |    |  |    |  |    |                          |
|----|--------------------------|----|--|----|--|----|--------------------------|
| AL | Albania                  | ES | Spain                                    | LS | Lesotho                                      | SI | Slovenia                 |
| AM | Armenia                  | FI | Finland                                  | LT | Lithuania                                    | SK | Slovakia                 |
| AT | Austria                  | FR | France                                   | LU | Luxembourg                                   | SN | Senegal                  |
| AU | Australia                | GA | Gabon                                    | LV | Latvia                                       | SZ | Swaziland                |
| AZ | Azerbaijan               | GB | United Kingdom                           | MC | Monaco                                       | TD | Chad                     |
| BA | Bosnia and Herzegovina   | GE | Georgia                                  | MD | Republic of Moldova                          | TG | Togo                     |
| BB | Barbados                 | GH | Ghana                                    | MG | Madagascar                                   | TJ | Tajikistan               |
| BE | Belgium                  | GN | Guinea                                   | MK | The former Yugoslav<br>Republic of Macedonia | TM | Turkmenistan             |
| BF | Burkina Faso             | GR | Greece                                   | ML | Mali   | TR | Turkey                   |
| BG | Bulgaria                 | HU | Hungary                                  | MN | Mongolia                                     | TT | Trinidad and Tobago      |
| BJ | Benin                    | IE | Ireland                                  | MR | Mauritania                                   | UA | Ukraine                  |
| BR | Brazil                   | IL | Israel                                   | MW | Malawi                                       | UG | Uganda                   |
| BY | Belarus                  | IS | Iceland                                  | MX | Mexico                                       | US | United States of America |
| CA | Canada                   | IT | Italy                                    | NE | Niger  | UZ | Uzbekistan               |
| CF | Central African Republic | JP | Japan                                    | NL | Netherlands                                  | VN | Viet Nam                 |
| CG | Congo                    | KE | Kenya                                    | NO | Norway                                       | YU | Yugoslavia               |
| CH | Switzerland              | KG | Kyrgyzstan                               | NZ | New Zealand                                  | ZW | Zimbabwe                 |
| CI | Côte d'Ivoire            | KP | Democratic People's<br>Republic of Korea | PL | Poland                                       |    |                          |
| CM | Cameroon                 | KR | Republic of Korea                        | PT | Portugal                                     |    |                          |
| CN | China                    | KZ | Kazakhstan                               | RO | Romania                                      |    |                          |
| CU | Cuba                     | LC | Saint Lucia                              | RU | Russian Federation                           |    |                          |
| CZ | Czech Republic           | LJ | Liechtenstein                            | SD | Sudan  |    |                          |
| DE | Germany                  | LK | Sri Lanka                                | SE | Sweden                                       |    |                          |
| DK | Denmark                  | LR | Liberia                                  | SG | Singapore                                    |    |                          |
| EE | Estonia                  |    |  |    |  |    |                          |

WO 99/34385

PCT/EP98/08403

## A FIELD ELECTRON EMITTER AND A METHOD FOR PRODUCING IT

### FIELD OF THE INVENTION

The present invention relates to a field electronic technology, and more precisely  
5 to a device for field electron emission, made of a material uniform in composition,  
comprising diamond particles, bonded by graphite-like carbon.

The present invention relates also to a method for producing a device for field  
electron emission, comprising forming an intermediate body of predetermined size  
10 and form from diamond particles, heat treating the intermediate body in a medium  
of gaseous hydrocarbon or hydrocarbons and making of shaped emitter surfaces  
in cases when it is necessary.

### BACKGROUND OF THE INVENTION

15 The materials with low threshold of field emission can be used in different  
electronic devices, such as efficient cathodes, e.g., for flat display computers and  
TV displays.

As it is disclosed in US Pat. No.5.709.577 previous electron emitters are often  
20 made of metal (such as Mo) or semiconductor (such as Si) with sharp tips in  
micrometer sizes. For these materials fairly good emission properties having the  
stability and reproducibility necessary for practical applications have been shown.  
However, the required control voltage required is relatively high because of their  
work functions. The high voltage operation increases the defeating instabilities due  
25 to ion bombardment and surface diffusion on the emitter tips and necessitates that  
high power densities are supplied from an external source to produce the required  
emission current density. The manufacturing of uniform sharp tips is difficult,  
tedious and expensive, especially over a large area. Furthermore these materials  
are vulnerable to ion bombardment, chemically active species and temperature  
30 extremes, which is a serious concern. Further, this patent includes discussion  
about diamond being a desirable material for field emitters due to its low or  
negative electron affinity and robust mechanical and chemical properties. Diamond  
offers substantial advantages for field emitters, but there is a need for diamond

WO 99/34385

PCT/EP98/08403

2

emitters capable of emission at yet lower voltages. For example, flat panel displays typically require current densities of at least  $0.1 \text{ mA/mm}^2$ . Low cost CMOS driver circuitry can be used in the display if such densities can be achieved with an applied voltage below  $25 \text{ V/}\mu\text{m}$  for the gap between the emitters and the gate. Good quality, intrinsic diamond can not, because of its insulating nature, emit electrons in a stable manner. Therefore diamonds are conventionally doped into n-type semiconductivity to take advantage of the low or negative electron affinity of diamond and to achieve low voltage emission. The n-type doping process has not been reliably achieved for diamond though. P-type semiconductive diamond is not helpful for low voltage emission because the energy levels filled with electrons are below the vacuum level in n-type diamond. Typically a field of more than  $70 \text{ V/}\mu\text{m}$  is needed for p-type semiconductivity diamond to generate an emission current density of  $0.1 \text{ mA/mm}^2$ .

Field emission devices employing diamond field emitters are disclosed, for example, in US Pat. No. 5,129,850 and 5,138,237 and in JP Pat. 08264111, all of which are incorporated herein in reference.

Electron. Lett., 27(1991), page 1459 discloses materials based on diamond having a low voltage emission. The known emitter is made as polycrystalline diamond film, synthesized by deposition from a gaseous phase.

J. de Physique 1V, C5 (1996), page 113 discloses a material based on diamond which has a high electrical conductivity. A thin metallic layer is applied on the diamond surface to increase the diamond electrical conduction.

Appl. Phys.Lett, 64 (1994), page 2742 also discloses a material based on diamond. Doping of diamond helps to increase the electrical conductivity of the diamond.

30

Graphite-diamond materials for cold cathodes are now developed for very wide application fields. Such materials can be used for traditional emission cathodes as for energetic-electron emitters. Energetic-electron emitters providing electrons having kinetic energies in the order of  $1 \text{ keV}$  without acceleration through vacuum.

WO 99/34385

PCT/EP98/08403

3

An average electric field of 105-1010 V/m applied across a layer of emissive cathode material accelerates the electrons inside the layer (US Pat. No. 5,729,094). Injection-enhancing contacts that are created by combining the emitter material (layered diamond and graphite) after annealing or by conventional dry anisotropic etching or ion bombardment techniques, are described in US Pat. No. 5,713,775.

Patent appl. WO 9718576, discloses diamond powder field emitters, such as an electron field emitter comprised of diamond powder prepared by shock synthesis and also a field-emitter cathode comprised of diamond powder prepared by shock synthesis attached to the surface of a substrate, by e.g. pressing it against a conductor or by creating a thin metal layer on the substrate.

A method for making electron emitters using ultra-fine (5-10,000 nm) diamond particles treated to enhance their capability for electron emission under low electric fields, is disclosed in US Pat. No. 5,709,577. Specifically, the diamond particles heat-treated by hydrogen plasma, allows the production of electron emission current density of at least 0.01 A/cm<sup>2</sup> at very low electric fields of 0.5-1.5 V/μm. The emitters are fabricated by suspending the diamond particles in an aqueous solution, applying the suspension as a coating onto a conducting substrate such as n-type Si or metal, and then subjecting the coated substrate to a plasma of hydrogen, preferably at temperatures above 300°C. for 30 minutes or longer.

The described methods provide emitters with low emission threshold. Methods for their production are very complex in apparatus and provide articles of small sizes. It is very difficult to have homogeneous properties on the surface.

US Pat. No. 5,602,439; the nearest prior art to the present invention, discloses an emitter comprising diamond and conductive carbon, preferably graphite. The emitter has a graphite-like substrate covered with a diamond or a diamond-like carbon coating. The emitter may also be graphite or carbon with embedded diamond.

WO 99/34385

PCT/EP98/08403

4

A manner of the production is to make a graphite-like substrate by processing carbon fibers with a diamond particle suspension (particles size of 0.25-1.0  $\mu\text{m}$ ) in organic solvent. Then the substrate is dried. Diamond or diamond-like film is deposited on the substrate prepared by plasma or chemical deposition from carbon containing gases. The produced emitter has a substrate with high electrical conductivity and a diamond layer on its surface. The emitter has good emission properties.

The known emitter material, consisting of a graphite-like substrate being a conductor and a diamond or diamond-like coating active in emission, is a gradient material. During all emission processes, a gradual destruction of the emission surface takes place. Low substrate and irregular distribution of diamond particles in the covering results in the changing of emitter parameters (film thickness, film roughness, substrate thickness, substrate electrical conductivity etc.). This causes fluctuations and decrease in the emission properties. The method for producing the known emitter is power consuming and rather complex apparatus is required. The process does not guarantee uniform deposition of diamond particles onto a rather irregular surface of carbon fibers. This results in irregular thickness of the diamond or diamond-like layer. The irregularity limits the surface area of emitters. The mentioned drawbacks prevent producing large articles with uniform composition.

Another manner is to mix e.g. graphite and diamond in a suitable binder material. After forming and curing of the binder material, the additional diamond surfaces may be exposed by treatment with a suitable etchant to remove binder and some graphite from outer diamond surfaces. However in the document there is no information about the technique and conditions of the production method. Therefore it is difficult to foresee the reality of preparing of such materials and their emission properties.

Field emitters with shaped surfaces are known. The J. Appl. Phys., v.47, 1976, p. 5248 discloses field emitters made of silicon, among them emitters with tips resulting from etching. Disadvantages with the method for producing the emitters is the demands for expensive equipment. It is very difficult to produce large cathodes with uniform properties. They are not stable at high electrical densities,

WO 99/34385

PCT/EP98/08403

5

and high fields are necessary for causing an emission. The known solution does not permit to produce emitters of desired shaped surface.

5 Fabrication of field emission cold cathodes with sharp emitters is disclosed in JP patent 08264111. The process involves immersing a Si substrate in a HF solution, the substrate having reverse-pyramid recesses at the sides of (111) phases, surface-roughening of the substrate by supersonic vibration in a micro-particle diamond-containing acetone solution, anisotropic etching of the substrate to make the recesses deeper and sharper, vapor depositing diamond into the recesses of  
10 the substrate, and subsequently removing the Si substrate. The process provides cold cathodes with sharp and compact emitters.

The drawbacks of this patent method are, complex technique of diamond deposition which limits the size of produced emitters and gives low electrical conductivity of diamond layers compared with that of graphite-like carbons. The  
15 latter limits emission current of emitter.

With the above described cathode materials as a background, the inventors has developed new field electron emitter materials consisting of diamond – graphite-like material, with uniform composition and without using layered or sandwich type  
20 structures, e.g. with coatings on substrates.

The object of the presented invention is to provide an field emitter combining low threshold of emission with high electrical conductivity, uniform surface properties and stable properties in the same time, capable of self-recovering.

25

A further object of the invention is to provide a process for producing the field electron emitter, simple in realization, which makes it possible to form large articles having desired shaped and controllable surface to obtain maximum increasing of emission.

30

WO 99/34385

PCT/EP98/08403

6

**SUMMARY OF THE INVENTION**

The object of the invention is obtained by a field electron emitter consisting of  
5 diamond and graphite-like carbon, characterised in that said emitter within its  
volume has a uniform composition of diamond particles bonded by graphite-like  
carbon.

In a preferred embodiment the content of graphite-like carbon is less than 35 wt %  
10 in the field electron emitter. The diamond particle size is less than 60  $\mu\text{m}$ , or  
preferably the diamond particle size is less than 20 nm or being in the interval of  
0.1-60  $\mu\text{m}$ , or being a mixture of sizes less than 20 nm and sizes ranging in the  
interval of 0.1-60.. Moreover, the emitter surface has at least one jut substantially  
15 having the form of a pyramid or a truncated pyramid or a cone or a truncated cone  
or a cylinder. The emitter surface can have at least two types of juts.

In an alternative the emitter surface has at least one tip.

The emitter surface provided with at least one jut, can have an additional tip or  
20 additional tips.

In a second embodiment the intermediate body is formed to have a non-shaped  
surface.

25 The invention relates also to a method for producing a field electron emitter,  
comprising forming an intermediate body and heat treating said body in a medium  
of carbon containing gases, characterised in that said intermediate body is formed  
in a size and form, which correspond to the desired size and form of the emitter,  
from diamond particles, and said heat treating is carried out in a medium of  
30 gaseous hydrocarbon or hydrocarbons.

In a preferred embodiment said intermediate body is formed on a substrate made  
of copper or silicon. Said substrate can be a shaped substrate so that the



WO 99/34385

PCT/EP98/08403

7

intermediate body is formed to have a surface with a specific desired shape, and have, at least, one pit substantially in the form of an inverted pyramid or an inverted truncated pyramid or an inverted cone or an inverted truncated cone or an inverted cylinder. Said shaped substrate can be made by pressing or by anisotropic chemical etching. A tip or several tips can be made on the emitter surface after said heat treating. Additional tip or tips can be made on said shaped emitter surface with a jut or juts, for example on the surface of the jut. The tip or tips can be made on the emitter surface or shaped emitter surface, by ion bombardment. Said ion bombardment can be carried out by nitrogen or argon or neon ions.

The heat treating step is stopped before the graphite-like carbon content produced by heat treating exceeds 50 % of the diamond weight.

Alternatively the intermediate body is formed on a non-shaped, substrate or without any substrate. In the latter case, after heat treating the intermediate body, the ready article can be treated additionally by a stream of charged ions with energy of 1-50 keV to form a tip structure on the surface.

## BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present invention will now be described by the following figures:

Fig. 1 shows emission current density vs electric field at increasing (marked with filled squares) and decreasing (marked with unfilled squares) electric field

Fig. 2 shows a scheme of the forming of a shaped emitter surface by using a pit etched substrate

Fig. 3 shows a field emitter with a shaped surface of pyramids in array (magnification x 335).

Fig. 4 shows emission current vs electric field for materials prepared in Example 3.

Fig. 5 shows a field emitter surface treated by nitrogen ion stream (magnification x 5360).

Fig. 6 shows emission current vs electric field after treating by nitrogen ion stream.

WO 99/34385

PCT/EP98/08403

8

Fig. 7 shows a field emitter surface before treating by nitrogen-ion stream, (magnification x 5360).

#### DESCRIPTION OF THE INVENTION

- 5 The essence of the present invention consists in that the diamond particles, being bonded by the graphite-like carbon matrix, provide rather low threshold of cold electron emission. The physical process of cold electron emission is determined by a strong local field at a electron emitting site, (it increases the emission).
- 10 Broad variation of the field emitter size and shape; from as small values as diamond particle sizes, through size and shape of juts sizes up to much larger; provides to maintain properties at predetermined interval of values.

The field electron emission process can be accompanied by a great change of the material structure at microlevel. Unlike the known solutions, the field emitter according to the present invention has uniform structure through its whole volume. Said structure provides stable emitter properties during the emission operation. In the process of gradual destruction of the emitting surface during the emission operation, new diamond particles of same size and volume concentration appear on the material surface, i.e. self-recovering of the surface takes place.

The emitter material and structure according to the present invention determine high field emitter strength, which prevents deformation of the emitter surface. Such deformation is typical, e.g. for single silicon crystals with tip-surface or layered structures consisting e.g. of emitter material coatings on substrates.

Unlike the known emitters, the emitter according to the present invention is made of a 'diamond - graphite-like carbon' composite and has the principal advantage of allowing arrangement of freely placed juts of a predetermined density per area unit.

Presence of the graphite-like carbon matrix improves significantly the emission process. It is due to high electrical conductivity of the carbon matrix, which not only

WO 99/34385

PCT/EP98/08403

9

connects diamond particles to form a coherent composite but also provides an uniform electron transfer in the emission zone, i.e. to each diamond particle on the material surface.

- 5 It should be noted that a high volume concentration of diamond particles in the material determines a very high volume concentration of emitting nuclei on the surface. Each nucleus is represented by a separate diamond particle, isolated from the other particles and yet connected with them by a current conductive contact, i.e. the graphite-like carbon matrix.
- 10 Simplicity of the production method makes it possible to form large articles, with easily controlled production of juts of micro-size to achieve maximal increasing of the electron field.
- 15 The produced emitter has low threshold of electron field emission. Changing of diamond and graphite-like carbon content in the material within the claimed ranges, as well as varying of the surface shape permits to control the emitter properties over a wide range. This ability to control the properties is very important, and required for optimizing the characteristics necessary for different
- 20 specific applications. This is the reason why the field emitter and the method for producing the field emitter according to the present invention can have a wide field of applications, and be used in various devices for different purposes when emitter properties are predetermined.
- 25 Subsequent improvement of the field emitter, without any change of its essence and basic properties, can be achieved by treating the surface, e.g. in a medium of microwave hydrogen plasma. This provides surface cleaning of the diamond particles in the surface layer from undesirable impurities.
- 30 Another improvement, is to use doped diamond powders, where the diamond has been doped (in the surface or within the volume) with doping atoms (for example of B, P, N, Al and other atoms of metals and nonmetals), that changes the electrical and emission characteristics of the material.

WO 99/34385

PCT/EP98/08403

## 10

The process for producing the field electron emitter comprises the following steps:

- forming diamond particles into an intermediate body, having a shape and size corresponding to the desired shape and size of the field emitter;
- heat treating the intermediate body in a medium of gaseous hydrocarbon or a mixture of hydrocarbons at a temperature exceeding the decomposition temperature for the hydrocarbon or hydrocarbons. The following hydrocarbons can be used: acetylene, methane, ethane, propane, pentane, hexane, benzene and their derivatives, and natural gas.

- 10 The emitter according to the present invention can be produced by forming an intermediate body made from diamond particles of sizes less than  $60\mu\text{m}$ , or preferably  $20\text{ nm}$  or ranging from  $0.1\mu\text{m}$  to  $60\mu\text{m}$ , or from a diamond particle mixture with sizes of less than  $20\text{ nm}$  and ranging from  $0.1\mu\text{m}$  to  $60\mu\text{m}$ . The diamond particles are formed by known methods into the intermediate body,
- 15 having a predetermined shape and size. It is possible to use temporary binders, e.g., ethyl alcohol, phenolic resin etc. It is also possible to form without using any binders, by pressing or other methods.

- When using diamond particles of sizes larger than  $60\mu\text{m}$  it is difficult to achieve
- 20 the desired uniform emission properties due to coarse structure of the material. Diamond particles with sizes ranging from  $20\text{ nm}$  to  $0.1\mu\text{m}$  are less preferable than others because there are no good classification methods for them.

- The formed intermediate body is exposed in a medium of gaseous hydrocarbon or hydrocarbons and heat treated at a temperature exceeding the decomposition temperature of the hydrocarbon or hydrocarbons. These steps can be carried out according to the disclosure of the PCT/SE96/01216. Under these conditions a chemical heterogeneous reaction takes place in the pores of the intermediate body resulting in formation of a carbon layer on the surface of the diamond particles.
- 25 The formed graphite-like carbon joins the diamond particles and produces a coherent composite where the graphite-like carbon serves as matrix. It is obvious from the description of the process, that the process provides uniform distribution of diamond particles throughout the surface of the final body, as well as uniform distribution of current conductive matrix in it.
- 30

WO 99/34385

PCT/EP98/08403

11

The intermediate body is being treated until the graphite-like carbon content is increased by less than about 50% of the diamond weight. The graphite-like carbon content is less than 35 wt %. Producing field emitters with a graphite-like carbon content more than 35 wt % is technically difficult.

The conductive matrix provides for equal potential in the diamond-matrix interfaces for all diamond particles, including those placed in the surface and emitting electrons (i.e., which emit electrons).

10

To produce a field emitter of desired size and shape, with a shaped surface and made of said material uniform in composition, comprising diamond particles bonded by said graphite-like carbon, a shaped substrate can be used. Said substrate has at least one pit of predetermined size, shape and arrangement.

15

The at least one pit on the shaped substrate, corresponding to a jut with size and shape and arrangement, may substantially have the form of an inverted pyramid, inverted truncated pyramid, inverted cone, inverted truncated cone or inverted cylinder. The substrate can be made of copper, silicon and other materials resistant in a medium of hydrocarbon or hydrocarbons.

20

The desired substrate shape can be made by; press forming pits of desired shape, size and arrangement; by anisotropic chemical etching; ion-ray treating; progressive methods of lithography; and other modern hardware.

25

Chemical or electrochemical etching or other accessible methods can be used to remove away the non-shaped or shaped substrate. Removing of the substrate can be carried out before or after heat treating the intermediate body in a medium of hydrocarbons.

30

Chemical or electrochemical etching or other accessible methods are used to remove the shaped substrate, after formation of the diamond – graphite like carbon composite on top of it. As a result a field emitter with a shaped surface is produced. The shape can be, for example, an array of pyramids.

WO 99/34385

PCT/EP98/08403

12

By using ion charged stream of nitrogen ions, neon ions and similar, tips can be prepared on the surface. The treating with ion charged stream is taking place until tips are formed on the substrate surface of the field emitter.

5

To provide a structure of a surface having a complex shape comprising juts and tips, a shaped composite of diamond and graphite-like carbon having juts can additionally be treated by ion charged stream (nitrogen, argon ion etc.). In this case it is preferable that the size of the juts is about 10-100 $\mu$ m, and of the tips about 1-10 $\mu$ m. The stream energy is of 1-50 keV. The ion stream treating is a known method and is disclosed, e.g., in US Pat. 5713775.

10

**The following examples characterize the essence of the present invention.**

15 Example 1.

For producing an field emitter having the shape of a tablet with a diameter of 20mm and a thickness of 1.4 mm, a powder of synthetic diamond with particle size of 0.1-1  $\mu$ m (ACM 1/0, GOST 9206-80) was used. The powder was mixed with a temporary binder - 25% alcohol solution of phenolic resin. The quantity of said temporary binder was 4% of the diamond weight. The mixture was formed by pressing in a press form. The tablet was placed on a bottom puncheon having smooth surface. The formed intermediate body was heat treated at 160°C during 3 hours to cure the temporary binder. After the heat treatment the intermediate body was placed in a quartz reactor to be heat treated in the medium of natural gas at T=800°C, until the graphite-like carbon weight content was about 25% of the diamond powder weight in the intermediate body. The process of forming the graphite-like carbon in the whole volume of the intermediate body provides an emitter material (diamond + graphite-like carbon) uniform in composition. Thus field electron emitter, having a flat surface, consists of a composite material, comprising diamond particles with size of 0.1-1.0  $\mu$ m and the graphite-like carbon. The graphite-like carbon content is 20 wt%.

25

30

Fig. 1 shows the emission current density vs the electric field at increasing (marked with filled squares) and decreasing (marked with unfilled squares)

WO 99/34385

PCT/EP98/08403

13

electrical field. The I-V curve is characterized by low emission threshold and high sensitivity from voltage – the current is increasing very fast when changing electrical field from 10 to 14 V/ $\mu$ m, The I-V curve is also characterized by the fact that there is practically no hysteresis. It is very important characteristic of a field  
5 electron emitter as the changing of current is under the effective control during increasing and decreasing of applied electrical field. The insert on Fig. 1 shows emission the current density vs the electric field plotted in Fowler-Nordheim coordinates. I-V curve has linear segment, corresponding to conditions of effective work function at  $\phi=0.2$  eV. This value shows that the prepared material, uniform in  
10 composition, function good as cold cathodes for different applications. The emission threshold value is shown in the Table.

#### Example 2.

An article in the form of a tablet with a diameter of 50 mm and thickness of 2 mm  
15 has been formed from a powder of synthetic diamond with particles size of less than 20 nm. The intermediate body was formed by pressing in a press form without temporary binder and with smooth puncheons. The formed intermediate body, having a flat surface, was heat treated in a medium of natural gas at 730°C until the graphite-like carbon weight content had increased by 25 % of the  
20 diamond powder weight in the intermediate body. The process of forming the graphite-like carbon in the whole volume of the intermediate body provides the emitter material being uniform in composition (diamond + graphite-like carbon). Thus the field electron emitter, having a flat surface and being a composite material, comprises diamond particles with size of less than 20 nm and the  
25 graphite-like carbon. The graphite-like carbon content is 20 wt%. Electrical specific resistivity of the emitter is 800 Ohm\*cm.

Effective electron emission from the material, uniform in composition, has been demonstrated under relatively low electrical field by research and measurement of the prepared field emitter. The emission threshold value is shown  
30 in the Table.

WO 99/34385

PCT/EP98/08403

14

## Example 3.

For producing an article having the shape of a parallelepiped, a powder of synthetic diamond was used with particle size of 0.1-1 $\mu$ m (ACM 1/0, GOST 9206-80). A Si-substrate was used for forming the surface of the final body. Said substrate had pits, shaped as pyramids with a base area of 50x50  $\mu$ m and a height of 35 $\mu$ m, made by wet selective etching. Said powder was mixed with the temporary binder - 25% alcohol solution of phenolic resin. The amount of said temporary binder was 4% of the diamond weight. The mixture was placed on the substrate surface by pressing in a press form. The substrate was placed on a bottom punchon with the substrate pits situated against the mixture. The intermediate body on the substrate was heat treated at T=160°C during 3 hours to harden the temporary binder. After the heat treatment the intermediate body on the substrate was placed in a quartz reactor to heat treat in the medium of natural gas at T=850°C until the graphite-like carbon weight content was 15% of the diamond powder weight in the intermediate body. After the heat treatment the substrate was removed by chemical etching in a medium of nitric and hydrofluoric acids. As a result, the substrate surface form was left on the surface of the final body. The process of depositing graphite-like carbon in the whole volume of the intermediate body provides a field emitter material uniform in composition (diamond + graphite-like carbon).

Fig. 2 shows a scheme of forming the shaped emitter surface using a pit etched substrate, where 1-pit etched substrate, 2-mixture of diamond particles and temporary binder, 3-intermediate body, 4-field emitter with a shaped surface.

The field electron emitter produced with a predetermined surface shape, is made of a composite material, comprising diamond particles with size of 0.1-1  $\mu$ m and the graphite-like carbon. The graphite-like carbon content is 13 wt%. Fig.3 presents the produced field emitter surface. It shows that the surface has the predetermined shape of pyramid array. Each pyramid has a base area of 50x50  $\mu$ m and a height of 35 $\mu$ m. Fig.4 shows the dependence of emission current vs electric field. The I-V curve is characterized by very low emission threshold, high voltage sensitivity and practically absent hysteresis. The emission threshold value is shown in the Table.



WO 99/34385

PCT/EP98/08403

15

#### Example 4.

For producing an emitter having the shape of a disk with a diameter of 20mm and a thickness of 1.4 mm, a powder of synthetic diamond was used with particle size of 3-5  $\mu\text{m}$  (ACM 5/3, GOST 9206-80). The powder was mixed with the temporary binder - 25% alcohol solution of phenolic resin. The quantity of said temporary binder was 4% of the diamond weight. The intermediate body formed was heat treated at 160°C during 3 hours to harden the temporary binder. After the heat treatment the intermediate body was placed in a quartz reactor to heat treat in a medium of natural gas at  $T=850^\circ\text{C}$  until the graphite-like carbon weight content is increased by 11% of the diamond powder weight in the intermediate body. Further the emitter was treated by nitrogen ion ( $\text{N}^+$ ) charged stream at the following conditions: Current = 1mA, energy = 15.5 keV, stream diameter = 6mm, duration of treating = 4 hours, dose of treating =  $3 \times 10^{20} \text{ cm}^{-2}$ . The process provides the emitter material uniform in composition (diamond + graphite-like carbon). The field electron emitter is made of the composite material, comprising diamond particles with size of 3-5  $\mu\text{m}$  and the graphite-like carbon. The graphite-like carbon content is 10wt%. The emitter comprises tips on its surface, formed by ion beam treatment. Fig.5 demonstrates the structure, having array of tips. Fig.6 shows the dependence of emission current vs electric field. The I-V curve is characterized by low emission threshold, high voltage sensitivity and practically absent hysteresis. The emission threshold value is shown in the Table. For comparison Fig.7 demonstrates the emitter surface before the ion bombardment.

The emitters according to Examples 1-4 have been investigated on their emission properties. The conditions: a tungsten anode was placed at a distance of 20-100  $\mu\text{m}$  from the surface in order to measure characteristics of electron emission in electric fields of intensity up to 200 V/ $\mu\text{m}$ , when emission current density ranges from 10 nA/ $\text{cm}^2$  till 1 A/ $\text{cm}^2$ , in  $10^{-7}$  Torr vacuum. The results of the investigations are shown in the Table.

WO 99/34385

PCT/EP98/08403

16

| Example no. | Current density<br>[ $\mu\text{A}/\text{cm}^2$ ] | Emission threshold<br>[V/ $\mu\text{m}$ ] |
|-------------|--|---|
| 1           | 10   | 10  |
| 2           | 10   | 25  |
| 3           | 10   | 3   |
| 4 (Fig.5)   | 10   | 6   |
| 4 (Fig.7)   | 10   | 18  |

In all examples the emission was characterized by the following:

- absence of avalanche jumps of emission current along ascending branches of current -voltage characteristics, i.e. in increasing and decreasing of voltage, (smooth controlled emission behavior)
- small hysteresis (practically absent hysteresis) between ascending and descending branches of current - voltage characteristics
- absence of drift of, i.e. changing during time of exposition, current - voltage characteristics during repeated cycling at different current densities ranging from  $10 \mu\text{m}/\text{cm}^2$  to  $1 \text{ A}/\text{cm}^2$
- emission current in a fixed field is stable (test during 2 hours at current density up to  $1 \text{ A}/\text{cm}^2$ ), after such exposure current - voltage characteristics remained constant
- high space uniformity of emission, variation of threshold emission field along the surface was of less 20%
- usage of shaped surface helps to reduce emission threshold at  $3 \text{ V}/\mu\text{m}$ .

Thus, the presented invention provides in comparison with known solutions a production method for a material, which in combination with a low emission threshold has the following advantages:

- stability and self-recovering of emission properties,
- uniform emission properties throughout the emitter surface,
- sufficiently high level of electrical conductivity necessary for emitters, makes possible to produce large area planar emitters.

WO 99/34385

PCT/EP98/08403

17

## CLAIMS

1. A field electron emitter consisting of diamond and graphite-like carbon,  
c h a r a c t e r i s e d in that said emitter within its volume has a uniform  
5 composition of diamond particles bonded by graphite-like carbon.
2. A field electron emitter according to Claim 1, c h a r a c t e r i s e d in that the  
content of graphite-like carbon is less than 35 wt %.
- 10 3. A field electron emitter according to Claim 1 or Claim 2, c h a r a c t e r i s e d  
in that the diamond particle size is less than 60  $\mu\text{m}$ , or preferably the diamond  
particle size is less than 20 nm or being in the interval of 0.1-60  $\mu\text{m}$ , or being a  
mixture of sizes less than 20 nm and sizes ranging in the interval of 0.1-60  $\mu\text{m}$ .
- 15 4. A field electron emitter according to any one of Claims 1-3, c h a r a c t e r i -  
s e d in that the emitter surface has at least one jut.
5. A field electron emitter according to Claim 4, c h a r a c t e r i s e d in that said  
jut substantially has the form of a pyramid or a truncated pyramid or a cone or a  
20 truncated cone or a cylinder.
6. A field electron emitter according to any one of Claims 4-5, c h a r a c t e r i -  
s e d in that the emitter surface has at least two types of juts.
- 25 7. A field electron emitter according to any one of Claims 1-3, c h a r a c t e r i -  
s e d in that the emitter surface has at least one tip.
8. A field electron emitter according to any one of claims 4-6, c h a r a c t e r i s e d  
in that the emitter surface provided with at least one jut, has additional tip or tips.
- 30 9. A method for producing a field electron emitter, comprising forming an  
intermediate body and heat treating said body in a medium of carbon containing  
gases, c h a r a c t e r i s e d in that said intermediate body is formed in a size and  
form, which correspond to the desired size and form of the emitter, from diamond

WO 99/34385

PCT/EP98/08403

18

particles, and said heat treating is carried out in a medium of gaseous hydrocarbon or hydrocarbons.

10. The method according to Claim 9, characterised in that said  
5 intermediate body is formed on a substrate.

11. The method according to Claims 9-10, characterised in that said intermediate body is formed on a shaped substrate.

10 12. The method according to any one of Claims 10-11, characterised in that said substrate is made of copper or silicon.

13. The method according to claim 11-12, characterised in that said shaped substrate has, at least, one pit substantially in the form of an inverted  
15 pyramid or an inverted truncated pyramid or an inverted cone or an inverted truncated cone or an inverted cylinder.

14 The method according to any one of claims 11-13, characterised in that said shaped substrate is made by pressing or by anisotropic chemical  
20 etching.

15. The method according to claim 9, characterised in that a tip or tips are made on the emitter surface after said heat treating.

25 16. A method for producing a field electron emitter according to claim 15, characterised in that on the said shaped emitter surface with a jut or juts, additional tip or tips are made.

17. The method according to claim 15-16, characterised in that the tip or  
30 tips are made on the emitter surface or shaped emitter surface, by ion bombardment.

18. The method according to claim 17, characterised in that said ion bombardment is carried out by nitrogen or argon or neon ions.

WO 99/34385

PCT/EP98/08403

19

19. The method according to claim 9, characterised in that said heat treating is stopped before the graphite-like carbon content produced by heat treating exceeds 50 % of the diamond weight.

5

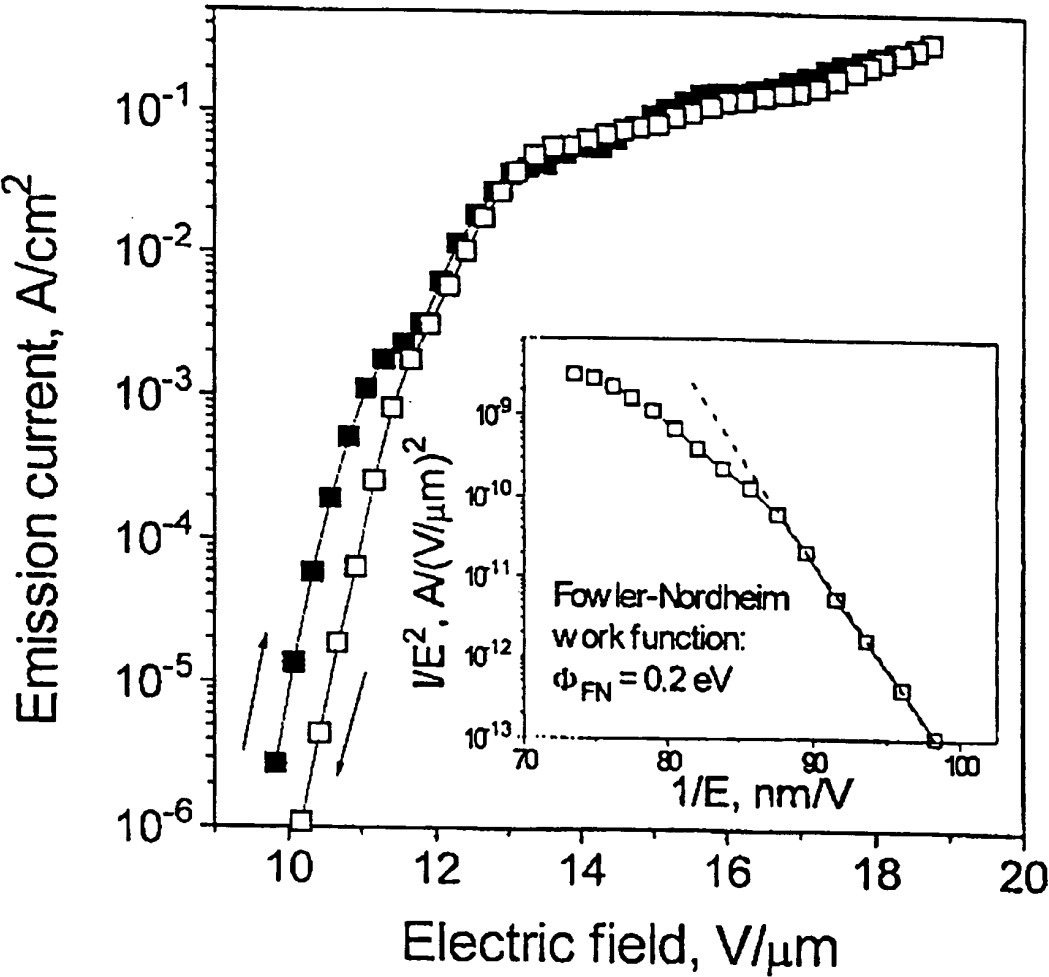


Fig.1

WO 99/34385

PCT/EP98/08403

2 / 7

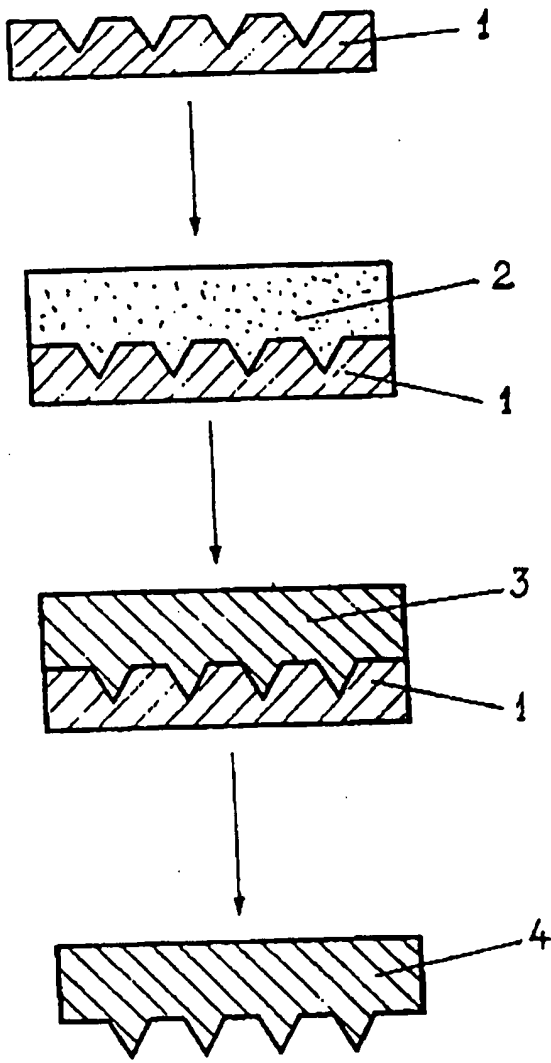


Fig.2

WO 99/34385

3 / 7

PCT/EP98/08403

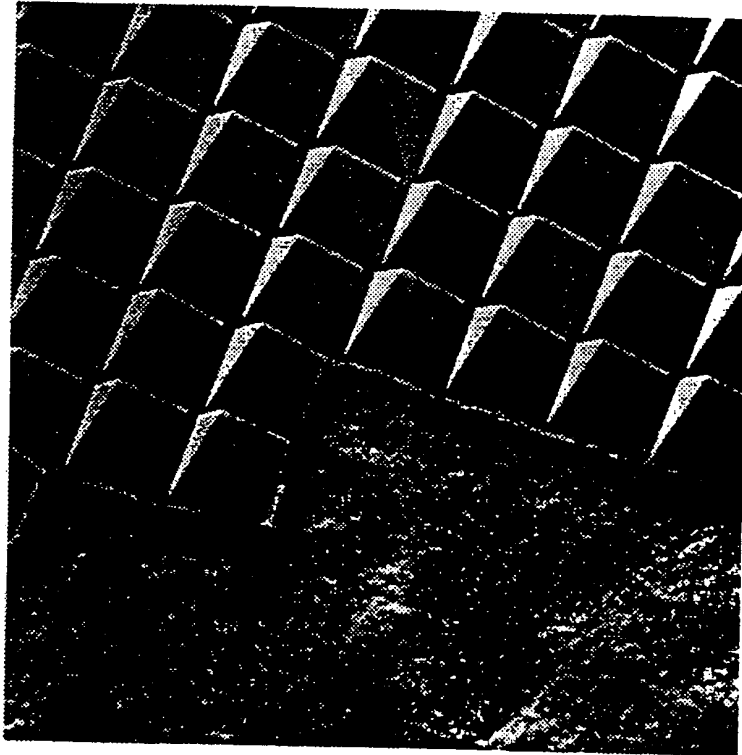


Fig. 3



WO 99/34385

PCT/EP98/08403

4 / 7

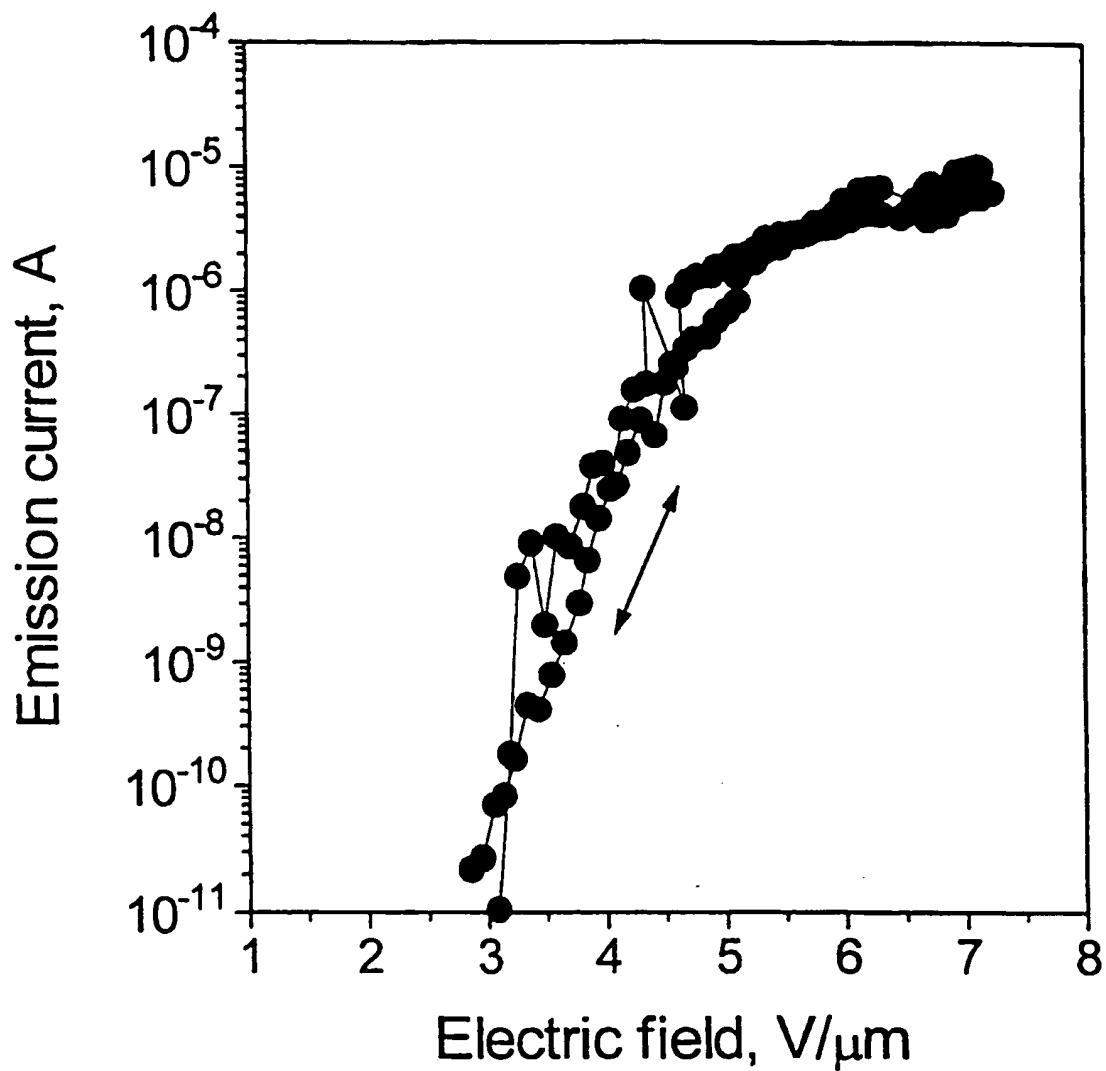


Fig.4

WO 99/34385

PCT/EP98/08403

5 / 7

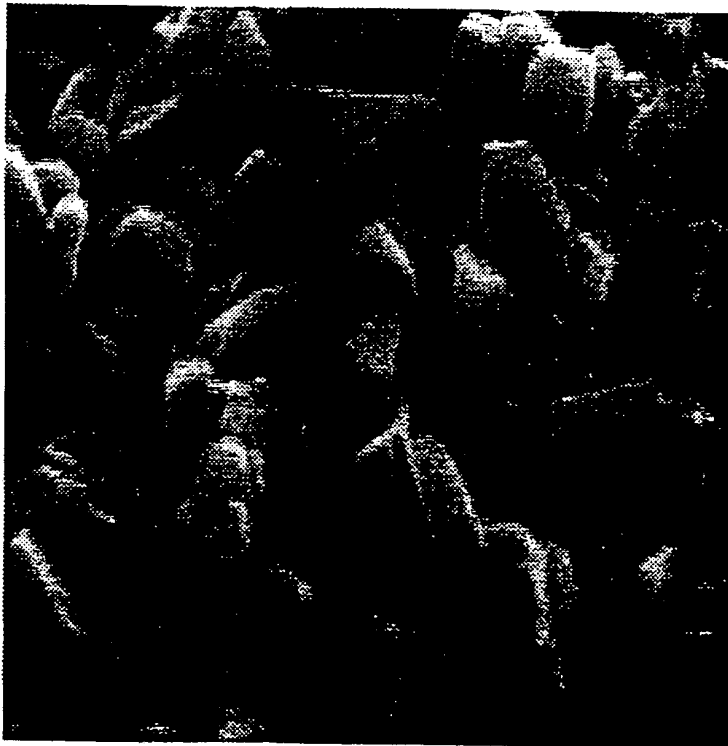


Fig. 5

WO 99/34385

PCT/EP98/08403

6 / 7

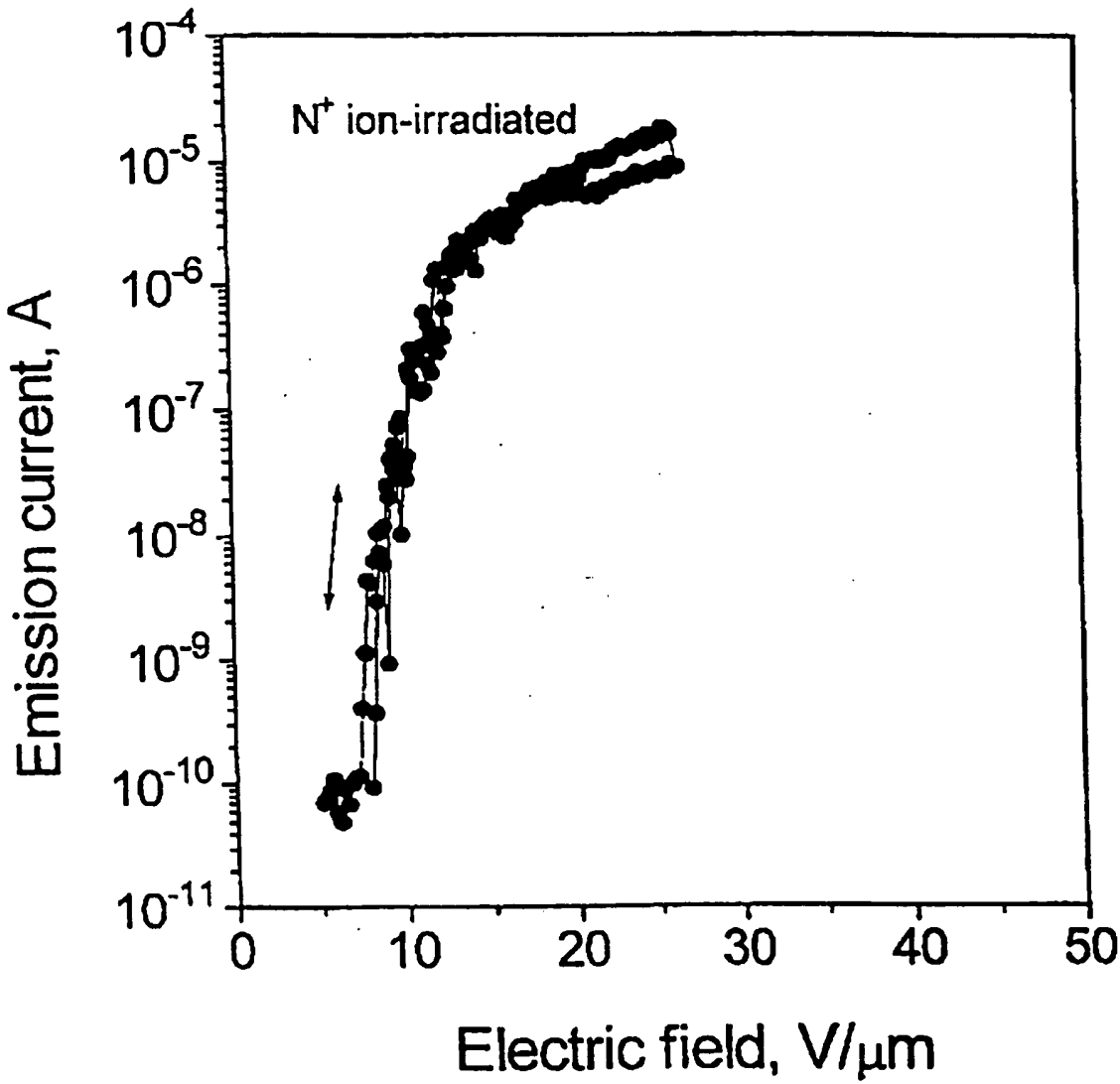


Fig.6

WO 99/34385

7 / 7

PCT/EP98/08403

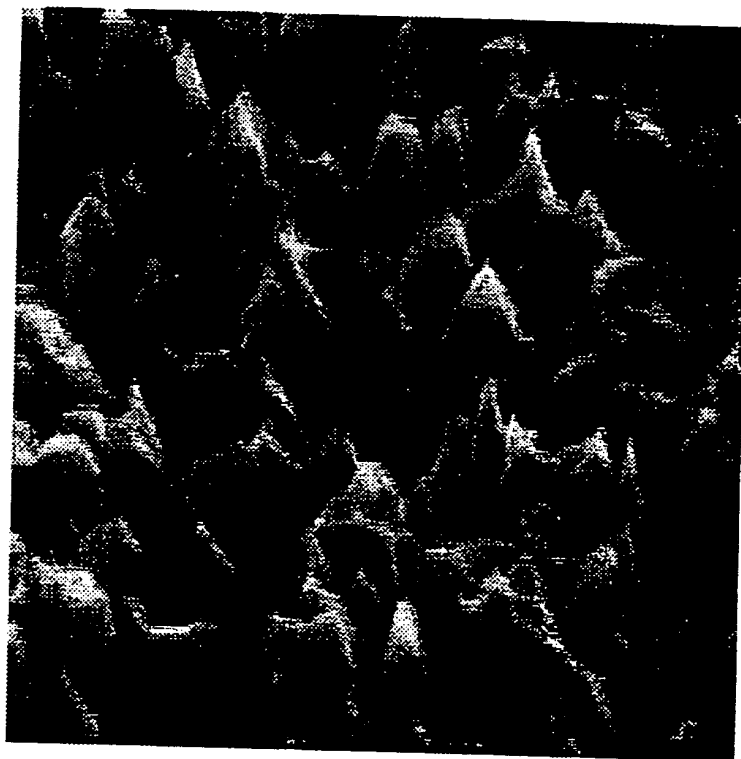


Fig. 7

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/08403

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01J1/30 H01J9/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| X          | WO 97 11923 A (ALFAR INT LTD ;BELOBROV<br>PETER IVANOVIETC (RU); DIKOV JURI<br>PAVLOVIE) 3 April 1997<br>cited in the application<br>see the whole document                                       | 9-11                  |
| A          | US 5 602 439 A (VALONE STEVEN M)<br>11 February 1997<br>cited in the application<br>see column 2, line 33 - line 41<br>see column 3, line 9 - line 39<br>see column 3, line 59 - column 4, line 2 | 1                     |

-/--



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

7 May 1999

Date of mailing of the international search report

17/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Colvin, G

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/08403

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT |   |                       |
|--|---|-----------------------|
| Category *   | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
| A  | WO 97 18576 A (DU PONT ;BLANCHET FINCHER<br>GRACIELA BEAT (US); SHAH SYED ISMAT ULLA)<br>22 May 1997<br>cited in the application<br>see page 2, line 36 - line 38<br>see page 5, line 15 - line 24<br>----- | 1                     |

INTERNATIONAL SEARCH REPORT

information on patent family members

|                              |
|------------------------------|
| International Application No |
| PCT/EP 98/08403              |

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---------------------|----------------------------|---------------------|
| WO 9711923 A                              | 03-04-1997          | RU 2093495 C               | 20-10-1997          |
|   |                     | AU 7103196 A               | 17-04-1997          |
|   |                     | CA 2231864 A               | 03-04-1997          |
|   |                     | CN 1198148 A               | 04-11-1998          |
|   |                     | EP 0852574 A               | 15-07-1998          |
| US 5602439 A                              | 11-02-1997          | AU 1843695 A               | 29-08-1995          |
|   |                     | WO 9522168 A               | 17-08-1995          |
| WO 9718576 A                              | 22-05-1997          | AU 7728696 A               | 05-06-1997          |

**THIS PAGE BLANK (USPTO)**



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**